

**Chemical Correlation of Some Late Cenozoic Tuffs  
of Northern and Central California by Neutron Activation  
Analysis of Glass and Comparison with  
X-Ray Fluorescence Analysis**

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GEOLOGICAL SURVEY PROFESSIONAL PAPER 1147



# **Chemical Correlation of Some Late Cenozoic Tuffs of Northern and Central California by Neutron Activation Analysis of Glass and Comparison with X-Ray Fluorescence Analysis**

*By* ANDREI M. SARNA-WOJCICKI, HARRY W. BOWMAN, *and* PAUL C. RUSSELL

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# Chemical Correlation of Some Late Cenozoic Tuffs of Northern and Central California by Neutron Activation Analysis of Glass and Comparison with X-Ray Fluorescence Analysis

By Andrei M. Sarna-Wojcicki, Harry W. Bowman, and Paul C. Russell

## ABSTRACT

Glasses separated from several dacitic and rhyolitic late Cenozoic tuffs of northern and central California were analyzed by neutron activation for more than 43 elemental abundances. Eighteen elements--scandium, manganese, iron, zinc, rubidium, cesium, barium, lanthanum, cerium, samarium, europium, terbium, dysprosium, ytterbium, hafnium, tantalum, thorium and uranium--were selected as most suitable for purposes of chemical correlation on the basis of their natural variability in silicic tuffs and the precision obtainable in analysis. Stratigraphic relations between tuffs and replicate chemical analyses on individual tuffs make it possible to calibrate a quantitative parameter, the similarity coefficient, which indicates the degree of correlation for the tuffs studied. The highest similarity coefficient (0.99) was obtained for analyses of two tuffs (potassium-argon dated at about 6.0 m.y.) exposed in the Merced(?) and Petaluma Formations of Sonoma County, which represent different paleoenvironments, shallow-water marine and fresh water or brackish marine, respectively. Correlation of these formations on the basis of criteria other than tephrochronology would be difficult. Results of neutron activation analysis in general confirm earlier correlations made on the basis of analysis by X-ray fluorescence but also make it possible to resolve small compositional differences between chemically similar tuffs in stratigraphic proximity. The Lawlor Tuff (potassium-argon dated at about 4.0 m.y.) is identified at two new localities: in a core sample obtained from a bore hole east of Suisun Bay, and from the Kettleman Hills of western San Joaquin Valley. This identification permits correlation of the uppermost part of the marine Etchegoin Formation in the San Joaquin Valley with the continental Livermore Gravels of Clark, the Tassajara Formation, and the upper part of the Sonoma Volcanics in the central Coast Ranges of California. A younger tuff near the top of the marine San Joaquin Formation in the Kettleman Hills has been identified at both new localities.

## INTRODUCTION

Within the past 14 years, a number of papers have been published on chemical correlation of volcanic ashes and tuffs (Czamanske and Porter, 1965; Jack and others, 1968; Lajoie and Carmichael, 1968; Jack and Carmichael, 1968; Izett and others, 1970; Borchardt and others, 1972; Randle and others, 1971; Dudas and others, 1973; Bartow and others, 1973; see also Westgate and Gold, 1974). The method has been shown to work well using a variety of analytical techniques and a number of elements. Most workers, however, have focused their attention on specific stratigraphic problems or the development of a particular analytical method. To this time, there has not been any

comparative evaluation of the different methods--which analytical method and what combination of elements work best to solve a particular problem. Nor has there been much statistical work done on the natural chemical variability of tephra--what differences exist within individual eruptive units, between eruptive units, and between units erupted from different volcanic provinces. Such studies can make correlations more definitive by defining the spectrum of compositional types, and they can help standardize analyses so that data collected by different workers can be used in making new correlations.

The present study has three purposes: to determine which elements are most suitable for chemical correlation using neutron activation analysis to calibrate quantitative parameters (similarity coefficients) that show correlation and provincial relations between tuffs, and to test by neutron activation analyses correlations made previously on the basis of X-ray fluorescence spectrometry (Sarna-Wojcicki, 1976).

**Acknowledgments.**--We are grateful to Douglas Hamilton of Earth Sciences Associates who provided core samples from the Collinsville area used in this study and to John Obradovich for providing information on tuffs in the Kettleman Hills.

## TUFF UNITS

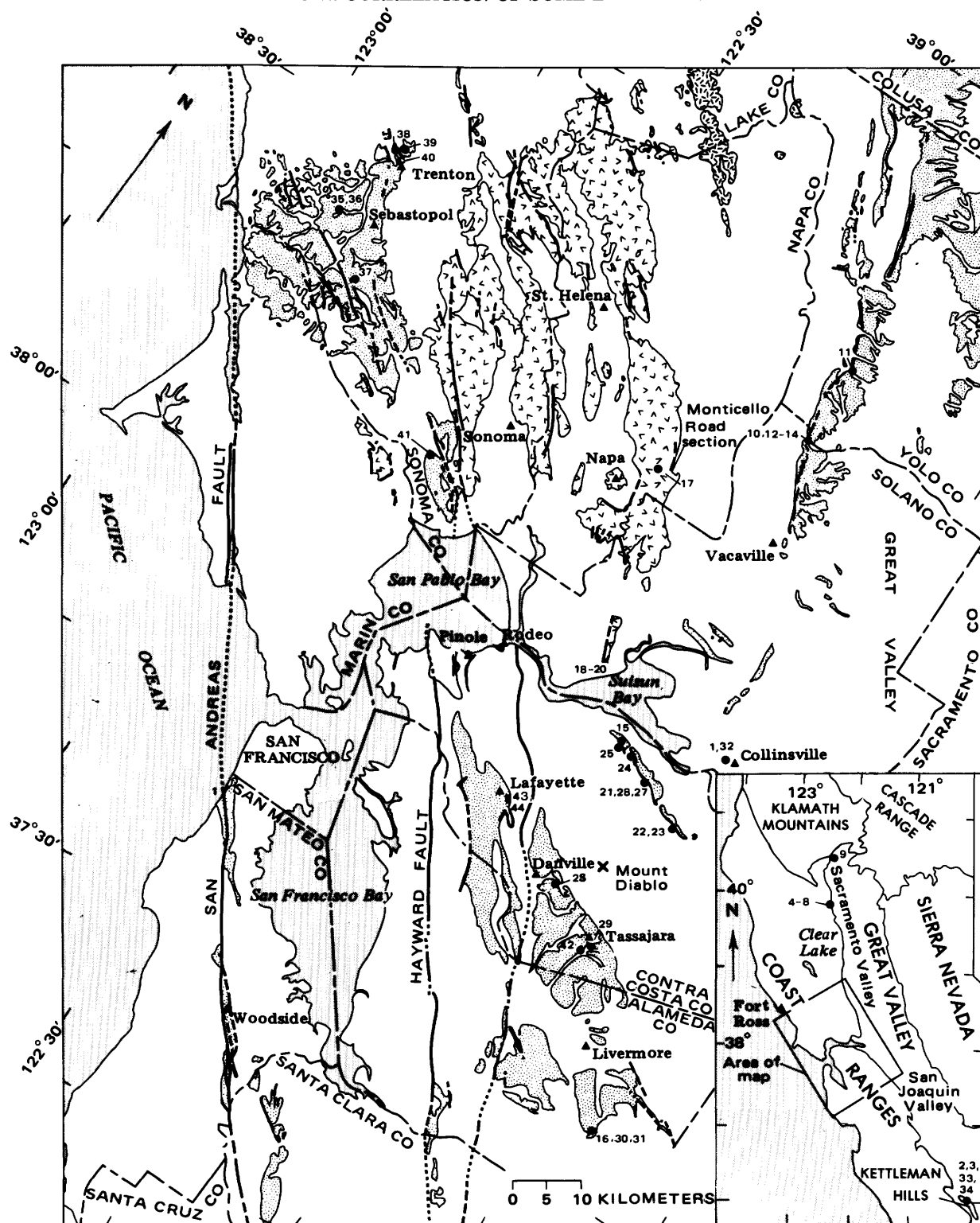
Tuff units studied were, from youngest to oldest: two thin tuffs in the uppermost part of the San Joaquin Formation, exposed in the Kettleman Hills of western San Joaquin Valley (samples 2 and 3) and the uppermost tuff in subsurface near Collinsville, east of Suisun Bay (sample 1); the Nomlaki Tuff Member of the Tehama Formation of northwestern Sacramento Valley (samples 4-9); the Putah Tuff Member (samples 10-15) of the Tehama Formation of southwestern Sacramento Valley, approximately the same age as the Nomlaki; the upper tuff in Livermore Gravels of Clark (1930) south of Livermore Valley (sample 16); the Lawlor Tuff, (samples 17-34); the tuff in the Merced(?) Formation of Sonoma County (samples 35-42); and the tuff above the Neroly Formation and below the Contra Costa Costa Group near Lafayette (samples 43, 44). Sample localities for these tuffs are shown in figure 1; their ages, stratigraphic positions, and earlier sources are summarized in table 1. Results of neutron activation analyses of glass samples of these tuffs are given in table 3, and results of X-ray fluorescence analyses are given in table 4. Note that some samples are analyzed only by neutron activation or X-ray fluorescence analysis and consequently are listed in only one of the two tables.

## SAMPLING METHODS

About 500 g of sample was collected from tuff outcrops. At some localities, several samples were collected vertically and laterally in each unit to test for compositional variations. At several localities, where two or more units are exposed in a stratigraphic sequence (for example, 1, 2, 15, 30), it was possible to test for compositional differences

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## CHEMICAL CORRELATION OF SOME LATE CENOZOIC TUFFS



## EXPLANATION

Late Cenozoic sedimentary deposits

Holocene to Pliocene(?)

Clear Lake volcanics

Pliocene

Sonoma volcanics

Major wide-spread tuff unit

Contact  
Major fault  
Dashed where approximately located;  
dotted where concealed

Sample locality

between tuffs of different ages. Replicate analyses of samples from individual units, together with analyses from multiple units in stratigraphic sequence, provide control for calibrating quantitative parameters such as the similarity coefficient of Borchardt, Aruscavage, and Millard (1972) that indicate correlation or its absence where stratigraphic control is not available.

## SAMPLE PREPARATION AND GLASS SEPARATIONS

Previous experience has shown that results of chemical analyses are markedly affected by the quality of glass separations (Sarna-Wojcicki, 1971, 1976). The presence of phenocryst, microlite, or lithic particles in glass separates can produce variations in trace-element composition owing to enrichment or depletion of many elements in these particles relative to glass (for example, concentrations of strontium and europium in plagioclase feldspar and iron, titanium, scandium, manganese, and zinc in amphiboles, pyroxenes and opaque minerals). Contamination by groundwater may cause similar variations in composition, such as in concentrations of strontium and barium as carbonates. Such variations are difficult or impossible to distinguish from differences due solely to variations in glass composition within and between individual tuff units. For this reason, glass separation is a critical laboratory procedure that requires great care.

Samples were disaggregated by hand or crushed in a mullite rotary crusher or mortar and sieved in plastic sieves with nylon screens. The 100-200-mesh size fraction<sup>1</sup> was treated with 10-percent reagent grade HCl, rinsed several times in distilled water, etched with 5-percent reagent grade HF, rinsed several times again, vibrated in an ultra-sonic probe, dried, and resieved. The sample was then separated in a Frantz magnetic separator and in acetone-bromoform and acetone-methylene iodide liquid mixtures utilizing a density-gradient column. For some samples, these procedures were repeated several times before a satisfactory separation was obtained.

<sup>1</sup>Initially, the 60-120-mesh size fraction was used; the smaller fraction was later chosen to reduce the number of glass shards containing phenocrysts and microlites. Size fractions finer than 200 mesh are difficult to work with owing to clumping during magnetic and heavy-liquid separations. The openings in nylon screens are somewhat smaller than those in equivalent mesh brass and stainless steel screens.

Figure 1.--Generalized geologic map showing location of samples, central Coast Ranges, California. Geology from Strand and Koenig (1965), Koenig (1963), Rogers (1966), Jennings and Burnett (1961), and Ross Wagner (written commun., 1974). Modified from Sarna-Wojcicki (1976).

## ANALYTICAL METHODS

### NEUTRON ACTIVATION ANALYSIS

When rock samples are irradiated with neutrons, many radioactive species are formed, and the mixture produces very complex gamma-ray spectra. The elemental sensitivities are directly related to the nuclear cross sections, and isotopic abundances inversely to radioactive half-lives, and vary considerably from element to element. Detailed computer analysis of these spectra can give very precise information on the abundances of a large number of elements. Using this method, we test for more than 50 elements, usually detect less than 40, and can actually use about 18 to 20 elements in correlation studies such as these.

Precision and sampling errors are tested at frequent intervals by analyzing a very homogeneous obsidian from Central America. The elemental precision for the 16 most precisely measured elements in this material varied from less than 1 percent to slightly more than 4 percent and resulted in an average standard deviation of 1.5 percent.

The accuracies here are controlled primarily by the uncertainties in chemical composition of our composite standard, a fired clay called "standard pottery." Many of the analytical procedures used in this study were originally developed during archeological studies of pottery types and their distributions in the Middle East (Perlman and Asaro, 1969). By our analysis of USGS standard rock G-2 by neutron activation analysis, using standard pottery as

Table 2.--Analyses of USGS standard rock G-2 by neutron activation and X-ray fluorescence

[Data for XRF analyses from Carmichael, Hempel, and Jack (1968). Iron in percent; other elements in ppm.]

Element	Average concentration (Flanagan, 1969)	Neutron activation (this study)	X-ray fluorescence (Carmichael and others, 1968)
Sc-----	3.9	3.70±0.07	---
Ti-----	2780	---	2930±3
Mn-----	260	250±7	280±5
Fe-----	1.85	1.90±0.04	1.84±0.02
Zn-----	85	97±15	80±2
Rb-----	168	185±20	175±2
Sr-----	479	---	465±2
Y-----	12	---	10±2
Zr-----	300	---	320±0
Cs-----	1.4	1.5±0.2	---
Ba-----	1870	1900±90	2030±20
La-----	96	91±2	110±10
Ce-----	150	166±5	175±10
Sm-----	7.3	7.0±1	10±5
Eu-----	1.5	1.36±0.05	---
Tb-----	.54	.5±0.1	---
Dy-----	2.6	2.5±0.2	---
Yb-----	.88	.84±0.03	---
Hf-----	7.35	8.4±0.7	---
Ta-----	.91	.74±0.02	---
Th-----	24.2	25.2±0.9	30±5
U-----	2.0	2.0±0.1	---



Table 1.--Age of tuff units studied  
[See figure 1 for locations of samples.]

Sample nos.		Neutron activation analysis (see table 3)	X-ray fluorescence analysis (see table 5); Sarna-Wojcicki (1976)	Unit	Geologic age	Radiometric age (K-Ar), in m.y.	References
1				Uppermost tuff in subsurface near Collinsville, east of Suisun Bay.	Pliocene or Pleistocene		Douglas Hamilton (oral commun., 1974).
2				Uppermost tuff in San Joaquin Formation, Kettleman Hills, San Joaquin Valley.	-----do.-----		Woodring, Stewart, and Richards (1940).
3				Next-to-uppermost tuff in San Joaquin Formation, Kettleman Hills, San Joaquin Valley.	-----do.-----		-----Do.-----
5, 6, 8, 9		4, 5, 6, 7		Nomlaki Tuff Member of Tehama Formation.	Pliocene	3.3±0.4	Russell (1931); Anderson and Russell (1939); Evernden, Savage Curtis, and James (1964) <sup>1</sup> ; Sims and Sarna-Wojcicki (1975); Sarna-Wojcicki (1976).
10, 13C, 13D		11, 12, 13		Putah Tuff Member of the Tehama Formation.	-----do.-----	3.3±0.1	Miller (1966) <sup>1</sup> ; Sims and Sarna-Wojcicki (1975); Sarna-Wojcicki (1976).
15		15		Tuff in lower part of Tehama Formation, south of Suisun Bay, above Lawlor Tuff.	-----do.-----		Sims and Sarna-Wojcicki (1975); Sarna-Wojcicki (1976).
16		16A, 16B		Upper tuff in Livermore Gravels of Clark (1930).	-----do.-----		Huey (1948); Sarna-Wojcicki (1971; 1976).
17, 23, 24, 31C, 31D, 32-34		17-31		Lawlor Tuff (type and tuffs at correlative localities.	-----do.-----	4.0±0.2, 4.0±1.0, 4.5±0.5	Huey (1948); Patten (1948); Weaver (1949); Oestreich (1958); Sarna-Wojcicki (1971, 1976) <sup>1</sup> .
38, 41C, 41D, 41E, 42		35-40, 41A, 41B, 42		Tuff in Merced(?) Formation of Sonoma County, Tuff in Petaluma Formation north of San Pablo Bay, and tuff near base of Tassajara Formation or top of Green Valley Formation of Clark (1943).	-----do.-----	5.7±0.5, 6.1±0.1	Clark (1943); Travis (1952); Weaver (1949); Bartow, Sarna-Wojcicki, Addicott, and Lajoie (1973) <sup>1</sup> ; Sarna-Wojcicki (1976) <sup>1</sup> .
44		43		Tuff above Neroly Formation below the Contra Costa Group, near Lafayette.	Miocene (?)	8.18±2.0	G. H. Curtis (oral commun., 1971) <sup>1</sup> Ross Wagner (written commun., 1974).

<sup>1</sup>Reference to radiometric age date.

the reference standard (table 2), other data presented here can be normalized to USGS preferred abundances of G-2.

Further information on the analytical method, including an explanation of the accuracies attainable, is given in Bowman, Asaro, and Perlman (1973).

### SAMPLE PREPARATION FOR NEUTRON

#### ACTIVATION ANALYSES AND MEASUREMENTS

Glass separates were ground to a powder and 100 mg mixed with 50 mg of cellulose binder and pressed into small pills. The pills were placed on edge in a radial array along with two identical standards and irradiated in the central thimble of the Berkeley Triga reactor for 18 minutes at  $1.7 \times 10^{12}$  ns/cm<sup>2</sup>, later for 8 hours at  $3 \times 10^{13}$  ns/cm<sup>2</sup>. The two standards were placed opposite each other, and the sample capsules rotated continuously during each bombardment.

Six different measurements were made on each unknown and standard set using various gamma-ray counting systems. For most analyses, samples were handled by automatic sample-changing equipment and the data, counting periods, dead-time counting rates, date, and time of the analysis recorded on magnetic tape. Computer programs determined the elemental abundances and errors by comparing the unknowns and the standard gamma-ray spectral data. Checks between individual analyses were made, as some elements were determined several times.

#### X-RAY FLUORESCENCE SPECTROMETRIC ANALYSES

Concentrations of trace and minor elements in glass separates were determined earlier (Sarna-Wojcicki, 1976) by means of a Norelco Universal Vacuum Spectrograph<sup>2</sup> using the analytical procedures described by Jack and Carmichael (1968). A detailed description of analytical methods is given in Sarna-Wojcicki (1971, 1976).

Glass samples were mixed with 20 percent by weight fibrous cellulose binder and pressed into 3.2-cm-diameter discs in a hydraulic press at pressures of about 2500 kg/cm<sup>2</sup>. The standards were similarly prepared in order to provide uniform surfaces for both sample and standard. Glass separates were then analyzed for titanium, manganese, iron, nickel, copper, zinc, gallium, rubidium, strontium, yttrium, zirconium, niobium, and barium. The position for each of these elements was calibrated with pure element standards, (for example RbCl for rubidium); element concentrations were determined by fixed-time counts at fixed 2θ positions. Additional counts were made at adjoining 2θ positions to determine the shape and intensity of the background curve. Standards used were G-1 and G-2 for all elements except gallium, zinc, copper, and nickel, for which W-1 was used (Fleisher, 1969; Flanagan, 1969).

## SELECTION OF ELEMENTS FOR CORRELATION

For the purpose of correlation, elements were selected on the basis of their variability within and between tuff units as well as according to the precision attainable for each element in neutron activation analysis. Independent stratigraphic evidence and radiometric age determinations make it possible to select the elements on the basis of their natural abundance and variability in tuffs and limitations of the analytical procedures used.

Eighteen elements--scandium, manganese, iron, zinc, rubidium, cesium, barium, lanthanum, cerium, samarium, europium, terbium, dysprosium, ytterbium, hafnium, tantalum, thorium, and uranium--were particularly useful in chemical correlation of silicic tephra in this study (table 3).

Six elements for which the analytical precision was about 12 percent or better--aluminum, sodium, potassium, cobalt, lutetium, and neodymium--were not included in calculations of similarity coefficients (below) because they do not provide adequate resolution for tephra units of different ages. Analytical error for the remaining 19 elements--magnesium, chlorine, calcium, titanium, vanadium, chromium, nickel, copper, gallium, arsenic, strontium, silver, indium, tin, antimony, tungsten, iridium, gold, and mercury--was greater than 12 percent of their average concentration in these silicic tuffs.

Of 13 elements analyzed by X-ray fluorescence in the previous study (Sarna-Wojcicki, 1976), 8 were used in correlation of tuff units: titanium, manganese, iron, zinc, rubidium, strontium, zirconium, and barium. The five elements not included were copper, nickel, gallium, yttrium, and niobium. Because some elements--manganese, iron, zinc, rubidium, and barium--were analyzed by both methods, it was possible to compare concentrations determined on splits of the same samples and to derive conversion factors from neutron activation to X-ray fluorescence analyses by least-squares plots.

## METHODS OF EVALUATING CHEMICAL DATA FOR USE IN CORRELATION

The degree of correlation between samples based on results of neutron activation analysis was determined graphically and numerically. First, concentrations of each of the eighteen elements used in correlation were ratioed to recommended concentrations of the same elements in USGS standard rock G-1, and histograms comparing sample pairs were made (fig. 2). Second, similarity coefficients have been calculated for every sample pair. This coefficient (Borchardt and others, 1972) is given by:

<sup>2</sup>Any use of trade names is for descriptive purposes only and does not constitute endorsement of these products by the U.S. Geological Survey.

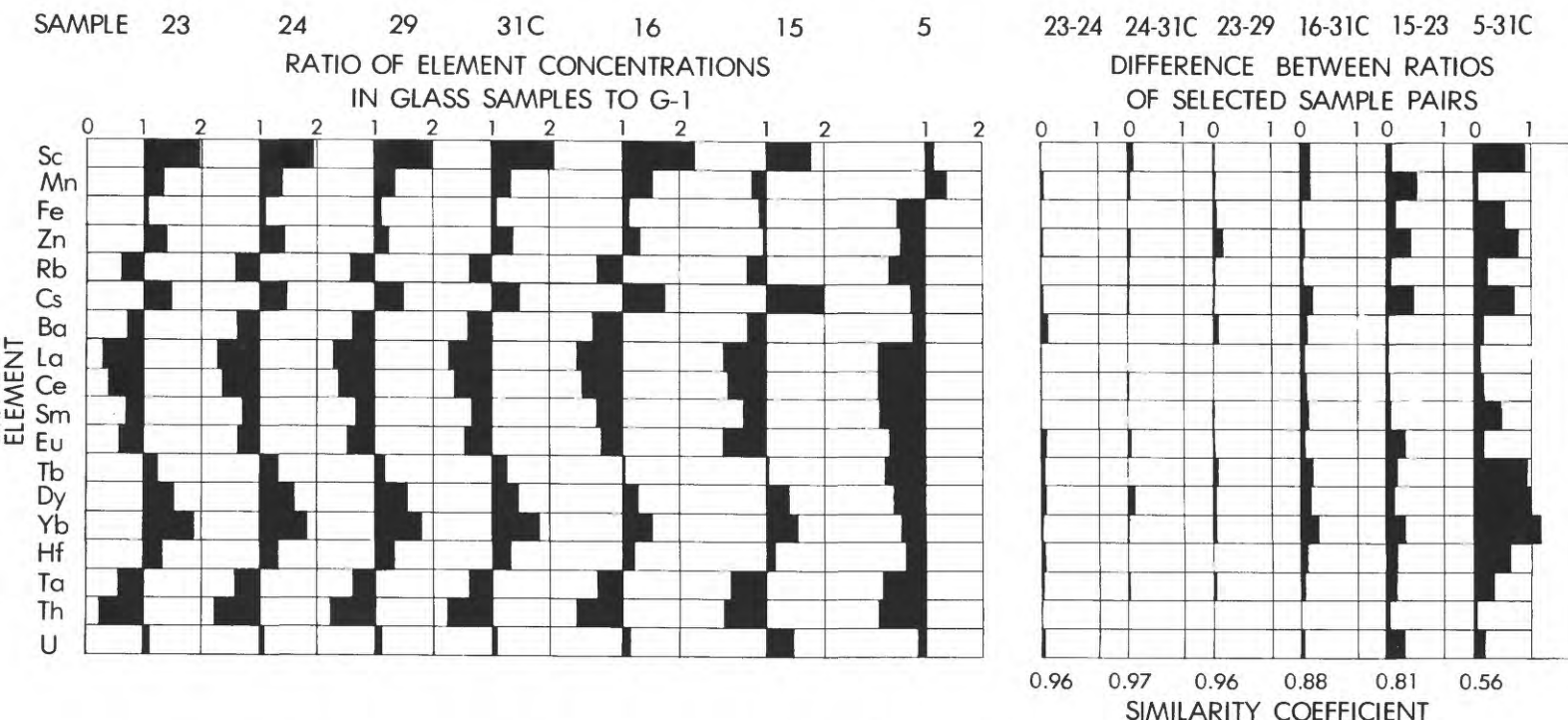


Figure 2.--Ratios of concentrations of elements in samples of volcanic glass to concentrations of the same elements in USGS standard rock G-1 are shown on the left side of the diagram. Absolute values of the differences of these ratios for selected sample pairs are shown on the right side of the diagram. Corresponding values of the similarity coefficient for these pairs are given below the right side of the diagram, beneath the corresponding sample pairs. Recommended values of G-1 (Fleisher, 1969) are used for all elements except for Cs, Tb, and Yb, to which values of 6, 1, and 2.5 parts per million, respectively, were assigned to avoid high ratios. Samples 23 and 24 are from the Lawlor Tuff. Samples 29 and 31C are correlated with the Lawlor Tuff on the basis of glass chemistry and other criteria (see text). Sample 16 is from a tuff which closely overlies the tuff containing sample 31C. Sample 15 is from a tuff correlated with the Putah Tuff Member of the Tehama Formation (Sarna-Wojcicki, 1976), which also overlies the Lawlor Tuff, but is considerably younger than both the Lawlor Tuff and the tuff overlying it (sample 16). All samples are from tuffs which were erupted in the Sonoma volcanic field, except for sample 5, from the Namlaki Tuff Member of the Tehama Formation, which was erupted from the southern Cascade Range volcanic field.

$$d(A.B.) = \frac{\sum_{i=1}^n R_i}{n},$$

where

$d(A.B.) = d(B.A.)$  = similarity coefficient for comparison between sample A and sample B,

$i$  = element number,

$n$  = number of elements,

$R_i$  =  $X_iA/X_iB$  if  $X_iB > X_iA$ ; otherwise  $X_iB/X_iA$ ,

$X_iA$  = concentration of element  $i$  in sample A, and

$X_iB$  = concentration of element  $i$  in sample B.

The value of the similarity coefficient for a chemically identical sample pair is 1. In practice, the value of the coefficient for replicate analyses of samples from a single outcrop, or of splits of the same sample, ranges from about 0.93 to 0.99 owing to inhomogeneities in the glass, slight variations in degree of separation of the glass, or analytical errors. For some of the earlier analyses of samples from the same outcrop, values of this coefficient are as low as 0.90, owing perhaps to incomplete separation of crystalline material from the glass. Values of similarity coefficients for tuff samples of demonstrably different age (for instance, tuffs superposed within a continuously exposed section) range from 0.45 to a high of 0.88. Since the ranges of replicate analyses from a single tuff generally do not overlap with those of tuffs of different ages, similarity coefficients can be used as quantitative guides to indicate correlation or its absence where stratigraphic control is not available.

As an example, let us consider the correlation of the Lawlor Tuff on the basis of its glass chemistry. Tuff samples taken from two outcrops of the Lawlor Tuff between which the tuff is continuously exposed (samples 23 and 24) show minor differences and a high similarity coefficient of 0.96 (fig. 2). A comparison of samples 23 and 29 reveals similar minor differences and the same similarity coefficient of 0.96 is calculated, although the tuff in this instance is not continuously exposed between these two localities (figs. 1 and 2). Since samples 23 and 29 are similar to the same extent as samples 23 and 24, they are here considered correlative and support an earlier correlation based on X-ray fluorescence analysis and petrographic criteria of the same samples (Sarna-Wojcicki, 1976). Independent evidence supporting this correlation comes from potassium-argon ages of the tuffs at localities 23 and 29 ( $4.0 \pm 0.2$ , and  $4.0 \pm 1.0$  m.y., respectively, Sarna-Wojcicki, 1976).

The Lawlor Tuff is also found further south in Livermore Valley, at locality 31. Sample 31 compares closely with the aforementioned Lawlor Tuff samples, the similarity coefficients for these comparisons being 0.97, 0.97 and 0.96. At locality 31, the Lawlor Tuff is overlain by a chemically and petrographically similar tuff (sample 16, table 3 and figs. 2 and 3). The similarity coefficient comparing the two superposed tuffs is 0.88. Analyses such as these on a number of superposed ashes and tuffs, combined with replicate analyses from individual units, have permitted calibration of similarity coefficients and make them a useful tool in evaluating tephrochronological data.

Within our experience, however, similarity coefficients for some tuff samples of different radiometric age erupted within the same volcanic province (for instance, the Putah Tuff Member of the Tehama Formation, potassium-argon dated at  $3.3 \pm 0.2$  m.y., and the tuff in the Merced(?) Formation of Sonoma County, potassium-argon dated at about 5.9 m.y.; see table 1) can be as high as 0.90. Consequently, similarity coefficients within the range 0.89-0.92 represent an interval of uncertainty and are

not by themselves considered to be conclusive evidence of correlation or its absence.

Since similarity coefficients of tuffs of different ages erupted within a single volcanic province or field (about 0.65-0.88) are generally lower than those of replicate analyses from the same unit but are higher than those of tuffs erupted from different volcanic fields (about 0.45-0.65), they provide a criterion for determining tuff or ash provenance. For instance, samples 5 and 31C (fig. 2) were erupted from different volcanic provinces. Their different origins are reflected in the glass chemistry of these two tuffs. Samples 15, 16, and samples of the Lawlor Tuff are from tuffs erupted from the same volcanic province, the Sonoma volcanic field, and bear a strong family resemblance to each other, a reflection of their common genesis (fig. 2).

The ranges of similarity coefficients given here apply only to units and volcanic areas studied by the neutron activation analytical method for the 18 elements used in the comparison procedure. Somewhat different values will be obtained if other units, analytical methods, or elements are used.

A matrix comparing values of similarity coefficients for all sample pairs in the study group was calculated. The relation of all analyzed samples with respect to the similarity coefficient is shown by a dendrogram (fig. 4) based on maximum individual values of similarity coefficients for sample pairs and maximum averages of coefficients for sample groups.

## CORRELATION OF SPECIFIC UNITS

A summary of correlations documented in this study is given in a correlation chart, fig. 4. Discussion of correlation of specific units, from oldest to youngest, follows.

### TUFF IN MERCED(?) FORMATION OF SONOMA COUNTY

Neutron activation analyses presented in this study confirm earlier correlations (Sarna-Wojcicki, 1976) of the tuff in the marine Merced(?) Formation of Sonoma County (loc. 38) with the tuff in the estuarine(?) Petaluma Formation near Sears Point (loc. 41, samples 41C, D, and E), and the tuff near the base of the continental Tassajara Formation or the top of the continental Green Valley Formation of Clark (1943) (loc. 42) (figs. 1 and 3). Ten similarity coefficients obtained from comparison of glass chemistry of samples pair range from 0.94 to 0.99 (fig. 4) with an average value of 0.96. Samples 41C, D, and E, replicate analyses of samples from a single outcrop in the Petaluma Formation, correlate at values of 0.95, 0.95, and 0.98, which also average 0.96. The highest similarity coefficient obtained in this study (0.99 for samples 38 and 41E, Fig. 4) is for tuff exposed at localities more than 60 km apart in two different formations representing two different depositional environments and facies, and consequently different faunal assemblages. Contact relations between the two formations are nowhere exposed, being either severed by faults or covered by younger alluvium.

Table 3--Neutron activation analyses of glass of tuffs

[Sample numbers are same as locality numbers shown in figure 1. Concentrations of iron in percent; all other concentrations in parts per million. Samples with letter designations (C, D, E) are replicate analyses of samples from a single locality, or of splits of the same sample.]

Sample	Sc	Mn	Fe	Zn	Rb	Cs	Ba	La	Ce	Sm	Eu	Th	Dy	Yb	Hf	Ta	Th	U
Uppermost ash in core near Collinsville, east of Suisun Bay(1), and uppermost ash in San Joaquin Formation, Kettleman Hills, San Joaquin Valley (2)																		
1	4.48	610	2.23	100	94	8.3	590	28.7	63.1	7.29	1.28	1.42	9.4	6.40	9.91	1.20	9.7	3.92
2	5.96	564	2.36	113	111	8.6	755	31.6	69.1	8.20	1.29	1.47	10.5	6.83	10.03	1.05	10.3	3.75
Next-to-uppermost ash in San Joaquin Formation, Kettleman Hills, San Joaquin Valley																		
3	7.50	508	2.21	99	125	10.1	804	34.2	72.8	8.17	1.15	1.54	10.3	6.56	10.40	1.01	12.5	4.69
Nomiaki Tuff Member of Tehama Formation, northwestern Sacramento Valley																		
5	3.52	317	0.74	27	89	4.7	959	19.7	35.7	2.19	0.51	0.34	2.4	1.56	3.96	0.44	10.7	3.52
6	3.69	324	.79	36	97	5.4	1145	21.4	40.1	2.39	.44	.30	2.3	1.91	4.06	.53	11.2	3.93
8	3.71	303	.76	36	104	5.1	1158	20.9	40.2	2.36	.47	.32	3.0	1.74	4.32	.53	11.1	3.76
9	3.63	330	.80	33	103	5.2	1013	20.7	40.8	2.36	.44	.33	2.3	1.90	4.26	.52	11.3	3.84
Upper beds of Putah Tuff Member of Tehama Formation, southwestern Sacramento Valley																		
10	7.09	192	1.13	57	165	11.7	832	30.0	67.2	6.39	0.39	1.14	7.7	4.75	7.29	0.84	14.6	5.22
13C	7.21	207	1.16	54	153	11.6	793	30.3	67.0	6.45	.35	1.15	7.6	5.02	7.22	.89	14.4	5.31
13D	7.15	197	1.18	49	160	11.7	864	30.4	65.5	6.56	.34	1.05	7.9	5.12	7.20	.80	14.5	5.40
Thin tuff in lower part of Tehama Formation above Lawlor Tuff south of Suisun Bay																		
15	5.30	181	1.21	44	159	12.0	857	29.6	60.1	5.64	0.38	1.04	7.0	3.84	6.95	0.65	15.7	5.77
Upper tuff in Livermore Gravels of Clark (1930) south of Livermore Valley																		
16	6.82	355	1.50	60	129	10.5	615	24.4	53.8	5.23	0.84	1.03	6.4	3.84	7.32	0.93	11.8	4.57
Lawlor Tuff (type and correlative localities)																		
17	6.08	327	1.48	68	134	9.1	794	32.1	65.5	6.50	0.71	1.16	7.6	4.93	7.85	0.92	12.8	4.56
23	5.89	305	1.45	64	139	9.0	881	32.2	67.0	6.50	.76	1.25	7.7	4.70	8.07	.94	13.0	4.43
24	5.86	319	1.46	65	137	8.8	759	30.5	66.9	6.38	.85	1.30	8.1	4.59	7.88	.98	12.9	4.32
29	5.93	312	1.50	56	129	8.9	750	31.2	66.2	6.28	.71	1.16	7.9	4.55	7.98	1.00	13.1	4.38
31C	6.22	309	1.47	63	141	9.0	755	31.3	69.3	6.41	.75	1.28	7.4	4.55	7.93	1.02	13.0	4.29
31D	6.17	330	1.47	61	137	9.2	788	32.7	69.6	6.61	.72	1.19	7.8	5.10	8.02	.96	13.1	4.50
32	6.23	328	1.35	76	149	9.4	800	31.9	70.7	6.66	.73	1.19	7.8	5.28	8.44	.99	13.7	4.59
33	5.88	322	1.47	69	129	9.9	752	31.7	68.4	6.42	.72	1.14	7.5	5.34	8.15	.97	13.0	4.48
34	5.91	326	1.51	68	127	9.8	763	33.3	67.5	6.54	.71	1.10	7.7	5.29	8.10	.96	13.4	4.49
Tuff in Merced(?) Formation of Sonoma County, in Petaluma Formation, and in base of Tassajara Formation or top of Green Valley Formation of Clark (1943)																		
38	4.28	188	1.00	42	158	13.7	720	29.1	58.9	4.79	0.34	0.81	5.6	3.86	6.16	0.82	14.9	5.90
41C	4.33	179	1.05	42	157	13.2	673	26.9	56.4	4.52	.31	.90	5.6	3.49	5.89	1.00	15.0	5.56
41D	4.31	185	1.05	45	167	13.6	700	27.9	59.0	4.81	.33	.85	5.6	3.88	6.23	.83	14.7	5.94
41E	4.28	184	1.02	43	163	13.7	715	28.4	59.4	4.78	.33	.78	5.6	3.79	6.02	.82	14.8	5.82
42	4.15	176	.99	39	153	12.4	707	27.9	55.7	4.58	.35	.86	6.0	3.26	5.79	.72	14.5	5.86

Table 3.--Neutron activation analyses of glass of tuffs--Cont.

Sample	Sc	Mn	Fe	Zn	Rb	Cs	Ba	La	Ce	Sm	Eu	Tb	Dy	Yb	Hf	Ta	Th	U
Tuff above Neroly Formation, below Contra Costa Group near Lafayette																		
44	5.47	184	1.05	46	132	13.7	637	32.2	70.2	6.20	0.35	1.10	7.4	4.99	6.72	0.99	15.4	6.19
Group averages																		
CORRELATION OF SPECIFIC UNITS																		
Uppermost ash in core near Collinsville, east of Suisun Bay (1), and uppermost ash in San Joaquin Formation, Kettleman Hills, San Joaquin Valley (2)																		
AVR.(2)	5.22	587	2.30	107	103	8.5	673	30.1	66.1	7.75	1.29	1.45	10.0	6.62	9.97	1.13	1.0	3.84
Next-to-uppermost ash in San Joaquin Formation, Kettleman Hills, San Joaquin Valley																		
3	7.50	508	2.21	99	125	10.1	804	34.2	72.8	8.17	1.15	1.54	10.2	6.56	10.40	1.01	12.5	4.69
Nomlaki Tuff Member of Tehama Formation, northwestern Sacramento Valley																		
AVR.(4)	3.64	319	0.77	33	98	5.1	1069	20.7	39.2	2.33	0.47	0.32	2.5	1.78	4.15	0.51	11.1	3.76
Upper beds of Putah Tuff Member of Tehama Formation, southwestern Sacramento Valley																		
AVR.(3)	7.15	199	1.16	53	159	11.7	830	30.2	66.6	6.67	0.36	1.11	7.7	4.96	7.24	0.84	14.5	5.31
Thin tuff in lower part of Tehama Formation and above Lawlor Tuff, south of Suisun Bay																		
15	5.30	181	1.21	44	159	12.0	857	29.6	60.1	5.64	0.38	1.04	7.0	3.84	6.95	0.65	15.7	5.77
Upper tuff in Livermore Gravels of Clark (1930), south of Livermore Valley																		
16	6.82	355	1.50	60	129	10.5	615	24.4	53.8	5.23	0.84	1.03	6.3	3.84	7.32	0.93	11.8	4.57
Lawlor Tuff (type and correlative localities)																		
AVR.(9)	6.02	319	1.46	66	136	9.2	782	31.9	67.9	6.48	0.74	1.20	7.7	4.93	8.05	0.97	13.1	4.45
Tuff in Merced(?) Formation of Sonoma County, in Petaluma Formation, and in base of Tassajara Formation or top of Green Valley Formation of Clark (1943)																		
AVR.(5)	4.27	182	1.02	42	160	13.3	703	28.0	57.9	4.70	0.33	0.84	5.7	3.66	6.02	0.84	14.8	5.82
Tuff above Neroly Formation, below the Contra Costa Group, near Lafayette																		
44	5.47	184	1.05	46	132	13.7	637	32.2	70.2	6.20	0.35	1.10	7.4	4.99	6.72	0.99	15.4	6.79
Average analytical error																		
	±0.03	±3	±0.02	±3	±7	±0.2	±20	±0.6	±0.6	±0.01	±0.02	±0.04	±0.1	±0.05	±0.09	±0.01	±0.2	±0.04

1-Samples analyzed by both NA and XRF analyses.

The tuff overlying the Neroly Formation and underlying the Contra Costa Group near the town of Lafayette at locality 44 (fig. 1), previously tentatively correlated with the tuff in the Merced(?) Formation of Sonoma County (Sarna-Wojcicki, 1976), does not correlate with that tuff or with any other unit in this study. Chemically, the tuff at locality 44 is most similar to the Putah Tuff Member of the Tehama Formation (similarity coefficients of 0.89 to 0.91) and the tuff in the Merced(?) Formation of Sonoma County (similarity coefficients of 0.85 to 0.88), (fig. 4). Stratigraphic and radiometric age data (table 1, fig. 3) together with earlier petrographic and X-ray fluorescence data (Sarna-Wojcicki, 1976), suggest that this tuff is as old or older than the tuff in the Merced(?) and much older than the Putah. Correlation of the tuff at locality 44 remains uncertain.

### LAWLOR TUFF

As mentioned earlier, sample 31 (C and D), from the lower tuff in the Livermore Gravels of Clark (1930) south of Livermore Valley (fig. 1), is correlated with samples 23, 24, and 29, the similarity coefficients being 0.97, 0.97 and 0.96, respectively (fig. 4). A potassium-argon age of  $4.5 \pm 0.5$  m.y. on the tuff at sample locality 31 compares closely with dates obtained at localities 23 and 29 ( $4.0 \pm 0.2$  and  $4.0 \pm 1.0$  m.y.).

A light-gray, water-deposited, water-transported(?) fine-grained vitric tuff (sample locs. 33 and 34) near the uppermost part of the Etchegoin Formation in the Kettleman Hills of western San Joaquin Valley (Woodring and others, 1940) is here correlated with the Lawlor Tuff (figs. 1 and 3). Trace- and minor-element chemistry of the glass in this tuff is essentially identical to that of the Lawlor and its other correlatives. Similarity coefficients between samples of the tuff in the Etchegoin Formation and samples of the Lawlor Tuff and its correlatives range from 0.94 to 0.97 with an average of 0.96 (fig 4).

A gray pumice-lapilli tuff, the middle one of three obtained from an exploratory bore hole near Collinsville east of Suisun Bay at a depth of 205 m (courtesy of Douglas Hamilton, Earth Science Associates), also correlates well with the Lawlor Tuff and its other correlatives. Similarity coefficients between the tuff from Collinsville (sample 32) and the Lawlor Tuff and other correlatives range from 0.93 to 0.96, with an average of 0.95.

In summary, the chemical data presented here make it possible temporally to correlate the uppermost part of the marine Etchegoin Formation of western San Joaquin Valley (locs. 33, 34) with certain formations in the central Coast Ranges: basal(?) lacustrine or alluvial deposits of the Livermore Gravels of Clark (1930) (loc. 31); alluvial gravels of the Tassajara Formation (loc. 29); the Lawlor Tuff south of Suisun Bay, which overlies the Neroly Formation and is overlain by the Tehama Formation (Sims and Sarna-Wojcicki, 1975) (locs. 23 and 24); unnamed alluvium in

the subsurface near Collinsville, east of Suisun Bay (loc. 32); and the upper part of the Sonoma Volcanics, north of San Pablo and Suisun Bays (loc. 17) (fig. 3).

These correlations illustrate advantage of the correlation method employed here. Samples 17, 23, 24, and 29 are from an ash-flow facies, sample 31 is from a water-laid lacustrine facies, and samples 33 and 34 are from a water-laid marine facies; all of these are now identified as the Lawlor Tuff. It would be difficult or impossible to make these correlations on the basis of field observations or paleontologic criteria alone.

At a locality south of Livermore, two tuffs (sample 16, is from the upper tuff, and samples 31, C and D, from the lower tuff) separated by about 8 m of tuffaceous deposits, are difficult to distinguish on the basis of X-ray fluorescence analysis or petrographic data (Sarna-Wojcicki, 1976) but are clearly distinguishable by chemical differences determined by neutron activation (table 3; figs. 2, 4). The similarity coefficients between sample 16 and 31 (C and D) are 0.88 and 0.88. The average of all similarity coefficients between sample 16 and samples of the Lawlor Tuff is also 0.88.

### NOMLAKI AND PUTAH TUFF MEMBERS

#### OF TEHAMA FORMATION

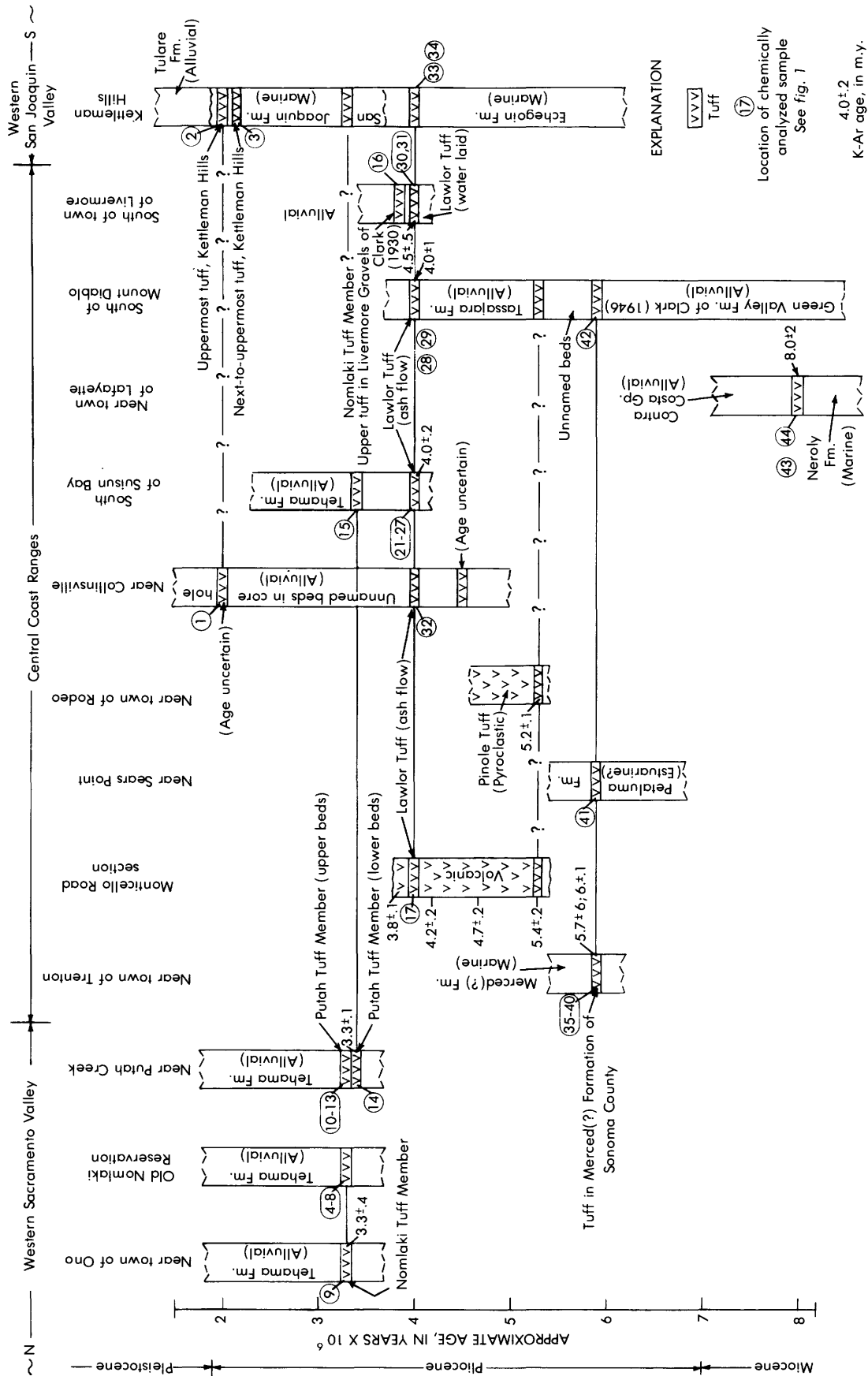
Three samples of the Nomlaki Tuff Member analyzed by neutron activation, samples 5, 6, and 8, are from a single outcrop at its type locality in the former Nomlaki Indian Reservation, but from different stratigraphic positions in the unit. Sample 9 is from a locality about 50 km farther north (fig. 1, inset map). Samples 6, 8, and 9 are very similar chemically (similarity coefficients of 0.95, 0.95, and 0.97, fig. 4). Sample 5, compared with 6, 8, and 9, has lower similarity coefficients (0.89, 0.90, and 0.91) perhaps owing to chemical inhomogeneities in the glass or to vertical variations within the Nomlaki Tuff Member, even though this unit appears to be texturally homogeneous. An alternative explanation is that the greater differences may result from inadequate separation of crystalline material from the glass, as sample 5 was one of the earlier samples processed in these studies (Sarna-Wojcicki, 1971; Sims and Sarna-Wojcicki, 1975; Sarna-Wojcicki, 1976), prior to several improvements in separation techniques.

Samples of the Putah Tuff Member analyzed by neutron activation, 10, 13C, and 13D, are from the type locality (fig. 1), a water-laid, composite unit probably produced by several eruptions within a short

Figure 3. Summary of correlation of late Cenozoic tuffs based on neutron activation analysis of glass. Solid horizontal lines indicate correlation certain; dashed horizontal lines, correlation probable; queries, correlation uncertain. Sample numbers are the same as in figure 1 and tables 3 and 4. For sources of potassium-argon ages, see Sarna-Wojcicki, (1976).

# NOMLAKI AND PUTAH TUFF MEMBERS

11





## CHEMICAL CORRELATION OF SOME LATE CENOZOIC TUFFS

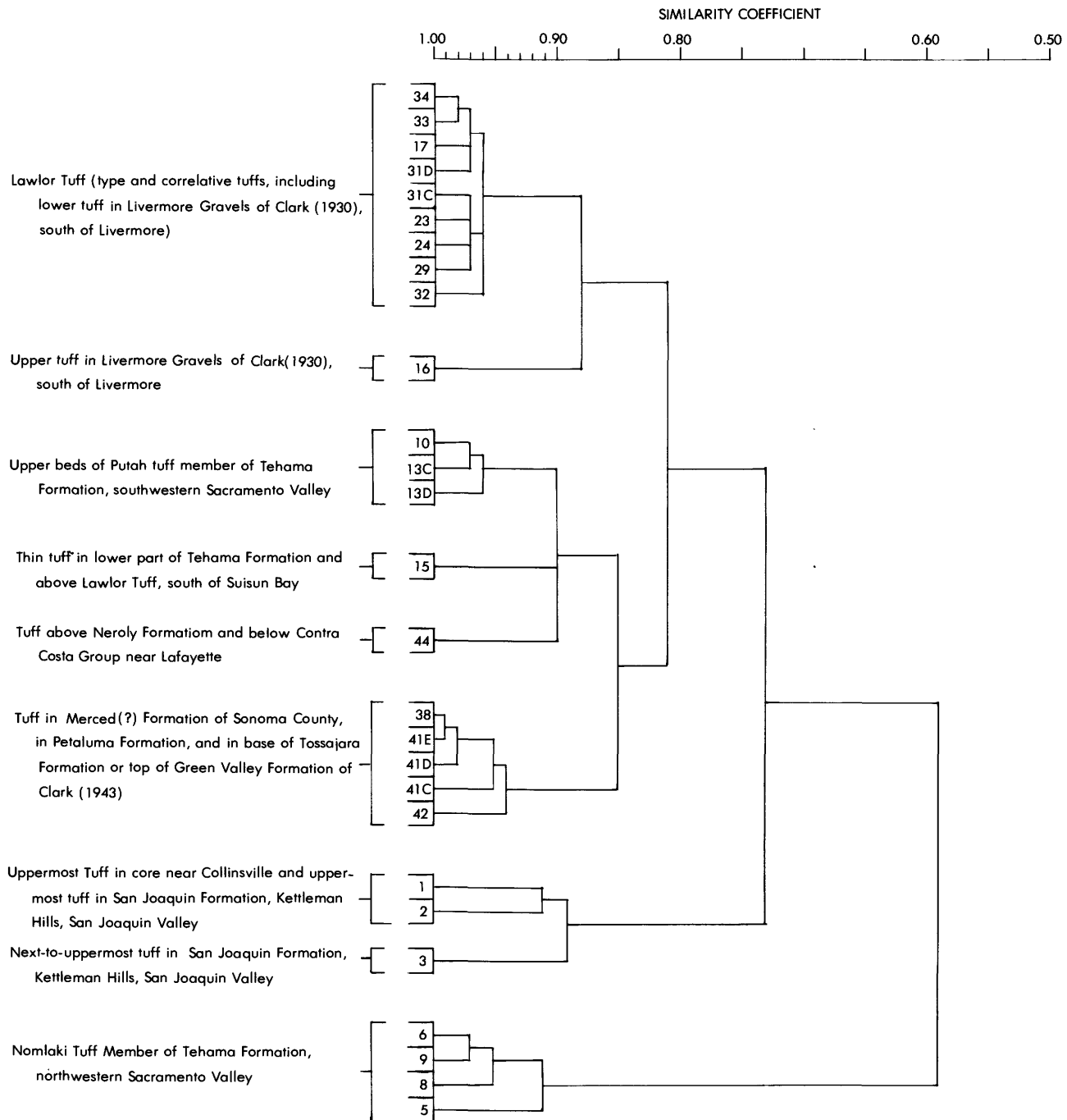


Figure 4.--Similarity coefficient dendrogram. Samples are grouped according to maximum individual values of similarity coefficients for sample pairs and maximum averages of coefficients for sample groups.

period. Values of the similarity coefficient of these three samples, all from the upper part of this unit, are 0.97, 0.96, and 0.96 (fig. 4). On the basis of X-ray fluorescence analysis of trace and minor elements of the glass and petrographic characteristics (Sims and Sarna-Wojcicki, 1975; Sarna-Wojcicki, 1976), the base of this unit (sample loc. 14) has been correlated with a thin tuff that overlies the Lawlor Tuff south of Suisun Bay (sample loc. 15, fig. 4). Since analyses by neutron activation have not been made on the basal part of the Putah, comparison of neutron activation and X-ray fluorescence analyses cannot be made for these samples.

#### TUFFS IN UPPERMOST PART OF SAN JOAQUIN FORMATION

Of two thin tuffs (locs. 2 and 3, fig. 1) in the uppermost part of the San Joaquin Formation in the Kettleman Hills, Kings County, the upper tuff (loc. 2) is chemically similar to a tuff (loc. 1) found in a core near Collinsville, Solano County, at a depth of 184 m below the surface (courtesy of Douglas Hamilton, Earth Science Associates). Sample 1 is more similar to sample 2 than to sample 3 (similarity coefficient 0.91, 0.86), but as similar to sample 3 as the two thin tuffs (samples 2 and 3) are to each other (similarity coefficient 0.91). These values of the similarity coefficient are too low to permit a definitive statement on the correlation of these units, but the similar stratigraphic position (above the Lawlor Tuff) of the tephra at both localities, combined with the unusual trace- and minor-element composition of the glass (high content of iron, manganese, zinc, europium, terbium, dysprosium, ytterbium and hafnium, table 3) suggests the possibility of a correlation between samples 1 and 2.

#### PROVINCIAL CHEMICAL CHARACTERISTICS OF SILICIC TEPHRA

Analyses of the Nomlaki and Putah Tuff Members of the Tehama Formation illustrate differences between silicic tephra units erupted from different volcanic fields. The Nomlaki Tuff Member (locs. 4-9), situated near the base of the Tehama Formation in northwestern Sacramento Valley, was erupted from a source northeast or east of Sacramento Valley, in the southern Cascade Range volcanic province (Anderson and Russell, 1939; Russell, 1931; Lydon, 1967). The Putah Tuff Member (locs. 10-14), also in the lower part of the Tehama Formation in southwestern Sacramento Valley, was erupted from a source in the central Coast Ranges (Miller, 1966), probably from the Sonoma volcanic field (Sims and Sarna-Wojcicki, 1975; Sarna-Wojcicki, 1976). The large differences in glass chemistry of these two units reflect differences in provenance and differences in the magmas from which the glass was derived. Similarity coefficients between samples of the Nomlaki and Putah Tuff Members range from 0.54 to 0.59 and average a low 0.57.

Tuffs erupted within the same volcanic field are chemically more similar than those erupted from different fields. Independent evidence regarding the

eruptive sources of some of the tuffs can be obtained from observations of changes in their stratigraphic thickness and textural gradients. For example, both the Lawlor Tuff and the Putah Tuff Member were erupted from the Sonoma volcanic field, as inferred from thickening of these units and increase in particle sizes toward this volcanic field. Chemical data from neutron activation analysis supports this interpretation since similarity coefficients between samples of these two tuffs are rather high, averaging 0.81 (fig. 4).

Other tuffs erupted in the Sonoma volcanic field, as inferred from physical evidence and glass chemistry, are the tuff (loc. 15) overlying the Lawlor Tuff (loc. 16) south of Livermore Valley, the tuff in the Merced(?) Formation of Sonoma County and its correlative tuffs (locs. 38, 41, 42), and the tuff overlying the Neroly Formation and underlying the Contra Costa Group near the town of Lafayette (loc. 44). The two thin tuffs near the top of the San Joaquin Formation in the Kettleman Hills (locs. 1 and 2) are more similar to the tuffs erupted from the Sonoma Volcanic field (similarity coefficients of 0.61 to 0.83) than to the Nomlaki Tuff Member (similarity coefficients of 0.48 to 0.54) and probably have been derived from this volcanic field.

#### COMPARISON OF ANALYSES BY X-RAY FLUORESCENCE AND NEUTRON ACTIVATION

A comparison of element concentrations determined by both neutron activation and X-ray fluorescence analyses for the same samples shows barium, rubidium, and zinc concentrations to be fairly similar, but large discrepancies exist for iron and manganese, both elements being consistently higher in the X-ray fluorescence analyses. These differences may be due to differences in standards or absorption corrections used in the two analytical procedures. (Absorption corrections were not used for iron and manganese in X-ray fluorescence analysis, since bulk compositions of samples and standards were approximately the same; Sarna-Wojcicki, 1971, 1976). Linear regression analyses indicate that best correspondence between X-ray fluorescence and neutron activation analyses was obtained for iron (correlation coefficient  $r^2$  of 0.98) followed by rubidium, barium, and zinc ( $r^2$  of 0.95, 0.95, and 0.92, respectively). Greater scatter of data was found for analyses of manganese ( $r^2$  of 0.82).

Although absolute concentrations of iron, manganese, and, to a lesser extent, rubidium differ between splits of the same samples, relative differences are about the same, and correlations based on neutron activation analyses are essentially the same as those based on X-ray fluorescence analyses. Somewhat better discrimination between units was obtained using neutron activation analysis, probably because a greater number of elements were analyzed and greater precision is obtained for some elements, permitting discrimination between chemically similar tuffs in stratigraphic proximity, for example, samples

Table 4.--Chemical analyses by X-ray fluorescence

[Sample numbers same as locality numbers in figure 1. Concentrations of Fe in percent; all others in parts per million. Samples with letter designations (A, B) are replicate analyses of samples from a single locality or of splits of the same sample. X-ray fluorescence data from Sarna-Wojcicki (1976). See table 2 for analytical error for these elements.]

Sample No.	Ti	Mn	Fe	Zn	Rb	Sr	Y	Zr	Ba
Nomlaki Tuff Member of Tehama Formation									
4	1332	419	0.94	33	107	169	12	182	1055
<sup>1</sup> 5	1372	518	.90	28	102	177	9	169	1052
<sup>1</sup> 6	1168	387	.87	28	103	162	14	181	965
7	1453	420	1.08	32	99	168	9	161	1003

## Upper beds of Putah Tuff Member of Tehama Formation

11	1131	244	1.40	37	158	68	24	263	981
12	1251	278	1.36	45	153	27	28	276	814
<sup>1</sup> 13	1088	262	1.34	43	174	35	27	256	794

## Lower beds of Putah Tuff Member of the Tehama Formation, and thin tuff in lower part of Tehama Formation, south of Suisun Bay

14	1018	244	1.39	39	170	37	21	261	838
<sup>1</sup> 15	1006	247	1.44	41	186	38	17	274	875

## Upper tuff in Livermore Gravels of Clark (1930) south of Livermore Valley

<sup>1</sup> 16A	1136	502	1.82	60	135	74	23	306	684
<sup>1</sup> 16B	1137	517	1.82	56	137	82	24	290	718

16 and 31C, D (fig. 2). Precision for analyses of titanium, zirconium, strontium, and yttrium, elements useful in correlation of silicic tephra, is greater in X-ray fluorescence than in neutron activation analysis.

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Table 4.--Continued.

Sample No.	Ti	Mn	Fe	Zn	Rb	Sr	Y	Zr	Ba
Lawlor Tuff									
<sup>1</sup> 17	1074	366	1.62	60	154	51	47	312	836
18	1174	459	1.73	58	154	59	26	326	817
19	1283	448	1.62	57	157	56	24	336	840
20	1473	436	1.75	59	143	68	27	339	801
21	1174	433	1.72	54	148	58	26	301	758
22	1211	440	1.72	57	145	50	24	297	812
<sup>1</sup> 23	1048	428	1.68	59	147	48	25	303	755

## Tuff in the Merced(?) Formation of Sonoma County, in Petaluma Formation, and in lower part of Tassajara Formation or top of Green Valley Formation of Clark (1943)

<sup>1</sup> 24	1180	470	1.81	63	149	62	25	304	796
25	1203	447	1.78	56	152	62	25	326	845
26	1173	437	1.73	59	143	54	18	329	830
27	1129	454	1.72	56	146	57	18	319	768
28	1258	456	1.68	67	144	71	32	313	913
<sup>1</sup> 29	1183	449	1.83	61	148	53	24	304	849
30	1134	422	1.70	59	148	71	29	305	809
<sup>1</sup> 31	1213	431	1.75	58	143	60	25	297	733
35	876	237	1.18	40	181	41	24	247	686
36	803	233	1.18	43	176	39	21	242	698
37	710	250	1.21	40	174	40	19	216	759
<sup>1</sup> 38	766	259	1.13	44	190	28	28	225	817
39	750	310	1.09	44	179	27	24	249	751
40	755	285	1.11	48	183	27	28	228	755
<sup>1</sup> 41A	729	278	1.07	41	181	44	23	221	724
<sup>1</sup> 41B	775	215	1.16	48	177	29	29	219	767
<sup>1</sup> 42	738	240	1.16	39	179	59	20	261	667

## Tuff above Neroly Formation and below the Contra Costa Group, near Lafayette

43	857	250	1.27	46	169	39	41	279	654
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<sup>1</sup>Sample analyzed by both neutron activation and X-ray fluorescence.

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